The shadowing effect in catalyst activity

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Throughout the years, the spatial arrangement of active material in a reactor bed and its effect on the observed reaction rates have been of interest in industrial catalysis [1] [2] and chemical physics [3] [4] [5]. Results have suggested that the observed activity is influenced by both the distance between active particles and transport phenomena. Transport limitations between neighboring catalyst particles induce a shadowing effect (SE) which limits the total exposure of the active particles to the diffusing reactant field, thus reducing catalytic activity. The dependence of this effect on particle placement is typically analyzed in chemical physics [6] [7]. More recently, particle shadowing has also been studied with the Temporal Analysis of Products (TAP) pulse-response technique [8], comprehending both experimental and theoretical studies [9] [10] [11]. However, experimental data had not yet systematically provided rigorous evidence of the universal existence of the SE. In this work, TAP experiments are performed in order to evaluate the influence of active particle inter-proximity on the apparent kinetics of CO oxidation over a $Pt/MgAl_2O_4$ catalyst. Using a fixed amount of catalyst particles, several reactor beds with varying degrees of particle dispersion and separation have been evaluated at different temperatures. Results consistently show increased CO conversion values as catalyst particles become increasingly more dispersed, thus serving as direct experimental evidence of the influence of the SE on catalyst activity. Furthermore, the dependence of the SE on the transport regime of the diffusing field was analyzed, with results showing that the SE is more significant under conditions that resemble Knudsen diffusion.

References

1. Van den Bleek, C.M et al. Chem. Eng. Sci. 24, 681 (1969).
2. Berger, R.J. et al. Chem. Eng. J. 90, 173 (2002).
3. Smoluchowski, M. Physik. Z., 17, 557 (1916).
4. Muthukumar, M. and Cukier, R.I. J. Stat. Phys. 26, 453 (1981).
5. Tsao, H., Lu, S. and Tseng, C. J. Chem. Phys. 115, 3827 (2001).
6. Deutch, J.M., Felderhof, B.U. and Saxton, M.J. J. Chem. Phys. 64, 4559 (1976).
7. Eun, C., Kekenes-Huskey P.M. and McCammon J.A. J. Chem. Phys. 139, 044117 (2013).
8. Gleaves, J.T., Ebner, J.R. and Kuechler, T.C. Catal. Rev. Sci. Eng. 30, 49 (1988).
9. X. Zheng et al. Appl. Catal., A 341, 86 (2002).
10. R. Feres et al. Chem. Eng. Sci. 64, 568 (2009).
11. M. Wallace et al. Comput. Chem. Eng. 125, 612 (2019).